METHODS AND COMPOSITIONS FOR CONTROLLING ALGAE

BACKGROUND

The present invention relates generally to the control of algae in bodies of water such as lakes, ponds and other aqueous systems. In one particular embodiment, the present invention relates to the control of such algae using bleaching pyridinecarboxamide compounds.

As further background, undesirable growth of algal species is a continuing challenge in water bodies such as lakes, ponds and reservoirs. To date, the primary agent used to control such algal species has been copper sulfate. Very few organic compounds have proven successful in this field.

One important issue faced when developing an algicidal agent for use in water bodies is the potential impact the agent may have on native aquatic plants. In many situations, maximal control of algae must be combined with minimal impact on native vascular plants.

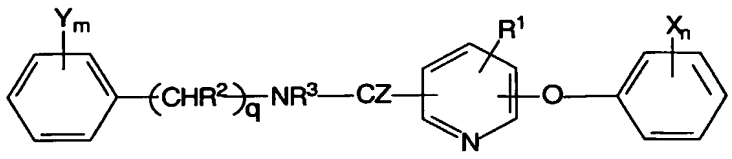
In light of this background, there is a continuing need for additional compositions and methods for selectively controlling algae. The present invention addresses this need.

SUMMARY OF THE INVENTION

It has been discovered that bleaching pyridinecarboxamide compounds can be used with advantage in the selective control of a broad range of algae in bodies of water such as lakes, ponds, reservoirs and the like. Accordingly, one preferred embodiment of the present invention provides a method for the selective control of algae in a body of water containing aquatic plants, comprising the step of providing in the body of water an effective algicidal concentration of a bleaching pyridinecarboxamide compound, and in one particular embodiment picolinafen. In general, methods of the invention will involve maintaining in the body of water a bleaching pyridinecarboxamide compound at a concentration of about 1 ppb to about 80 ppb, more typically about 1 ppb to about 30 ppb. The pyridinecarboxamide compound can be added to the body of water, for example, in liquid formulations. Using the preferred pyridinecarboxamide compounds, for example picolinafen, it has been found that there is substantially no impact upon aquatic plants in the treated body of water. In this regard, native aquatic plants typical to such bodies of water may include one or more of variable leaf pondweed (*Potamogeton diversifolious*), Illinois pondweed (*Potamogeton illinoensis*), coontail (*Ceratophyllum demeresum*),. Variable leaf milfoil (*Myriophyllum heterophyllum*), cone-spur bladderwort (*Utricularia*

gibba). common elodea (*Elodea canadensis*), spatterdock (*Nuphar luteum*) and water-lily (*Nymphaea* spp.).

Preferred pyridinecarboxamide compounds useful in the present invention are encompassed by the general formula:



wherein: R^1 is hydrogen, halogen, alkyl or haloalkyl;
R^2 is hydrogen or alkyl;
R^3 is hydrogen, alkyl, or alkenyl;
each X is independently a halogen atom, optionally substituted alkyl or alkoxy, alkenyloxy, alkynyloxy, cyano, carboxy, alkoxycarbony, (alkylthio)carbonyl, alkylcarbonyl, amido, alkylamido, nitro, alkylthio, haloalkylthio, alkenylthio, alkynylthio, alkylsulphinyl, alkylsulphonyl, alkyloximinoalkyl or alkenyloximinoalkyl;
each Y is independently a halogen atom, alkyl, nitro,cyano, haloalkyl, alkoxy or haloalkoxy;
Z is an oxygen atom or sulfur atom;.

n and m are independently 0 or an integer from 1 to 5; and
q is 0 or 1.

Particularly preferred among these compounds are the encompassed N-phenyl-4-phenoxy-3-pyridinecarboxamide compounds, N-phenyl-2-phenoxy-3-pyridinecarboxamide compounds, and N-phenyl-2-phenoxy-6-pyridinecarboxamide compounds.

Another preferred embodiment of the invention provides an algicidal concentrate composition for addition to a body of water for algae control, comprising a liquid carrier suitable for introduction into an aquatic environment, and a bleaching pyridinecarboxamide compound at level constituting about 5% to about 90% by weight of the overall composition, more typically about 10% to about 85% by weight of the overall composition. Such compositions and other compositions for use in methods of the invention can be provided in containers labeled with indicia for algicidal use, including for instance rates of application, etc.

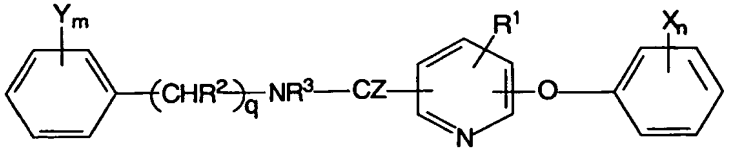
The present invention provides improved and/or alternative methods and compositions for controlling algal growth. Additional features and embodiment of the invention will be apparent from the descriptions herein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to certain embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and further applications of the principles of the invention as described herein being contemplated as would normally occur to one skilled in the art to which the invention relates.

As disclosed above, it has been discovered that bleaching pyridinecarboxamide compounds can be used to selectively control algae in bodies of water, including such bodies also containing aquatic plants. The present invention thus provides algicidal methods and compositions incorporating the use of such pyridinecarboxamide compounds.

Turning now to a discussion of algicidal agents for use in the invention, generally, they will belong to the class of bleaching pyridinecarboxamide compounds, some of which have been used in the past as herbicidal agents. Preferred bleaching pyridinecarboxamide compounds for use in the invention are encompassed by the formula I:



wherein: R^1 is hydrogen, halogen, alkyl or haloalkyl;
R^2 is hydrogen or alkyl;
R^3 is hydrogen, alkyl, or alkenyl;
each X is independently a halogen atom, optionally substituted alkyl or alkoxy, alkenyloxy, alkynyloxy, cyano, carboxy, alkoxycarbony, (alkylthio)carbonyl, alkylcarbonyl, amido, alkylamido, nitro, alkylthio, haloalkylthio, alkenylthio, alkynylthio, alkylsulphinyl, alkylsulphonyl, alkyloximinoalkyl or alkenyloximinoalkyl;
each Y is independently a halogen atom, alkyl, nitro,cyano, haloalkyl, alkoxy or haloalkoxy;
Z is an oxygen atom or sulfur atom;.
n and m are independently 0 or an integer from 1 to 5; and
q is 0 or 1.

The term alkyl as used herein in respect of a radical or moiety refers to a straight or branched chain radical or moiety. Suitably an alkyl moiety has from 1 to 6 carbon atoms, preferably from 1 to 4 carbon

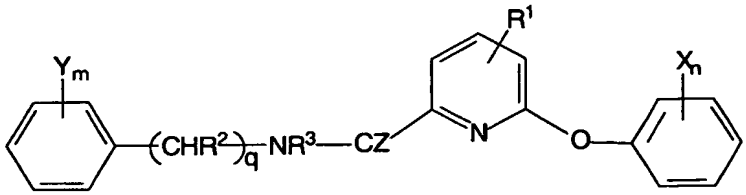
atoms. A preferred alkyl moiety is an ethyl or, especially, a methyl group and a preferred alkoxy moiety is ethoxy, especially, methoxy.

Unless otherwise noted herein, when an alkyl or alkoxy group is designated as being optionally substituted, the substituent groups which are optionally present may be any of those customarily employed in the development of biocidal compounds, and/or the modification of such compounds to influence their structure/activity, persistence, penetration or other property. Specific examples of such substituents include halogen, especially fluorine, chlorine or bromine atoms, and phenyl, cyano, amino, hydroxy, alkoxy and (alkyl)amino groups, alkyl groups suitably having 1 or 2 carbon atoms. Preferred substituents are halogen, especially fluorine, atoms.

As used herein the term halogen atom may denote a bromine, iodine, chlorine or fluorine atom, and is preferably a chlorine or fluorine atom, most preferably a fluorine atom.

Particularly preferred among the compounds of formula I are the N-phenyl-4-phenoxy-3-pyridine carboxamide compounds, N-phenyl-2-phenoxy-3-pyridine carboxamide compounds, and N-phenyl-2-phenoxy-6-pyridine carboxamide compounds.

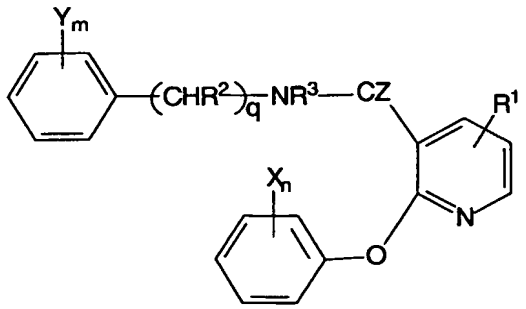
For example, suitable for use in the present invention are the compounds disclosed in U.S. Patent No. 5,294,597 issued March 15, 1994. Thus, the compounds may be encompassed by the general formula II:



wherein the variables R^1, R^2, R^3, X, Y, q, m, n and Z are as disclosed above. A further preference exists for compounds in which Z is an oxygen atom, m = 1, Y is fluorine (especially where Y_m represents 4-flouro), n = 1, X is trifluoromethyl (especially where X_n represents 3-trifluoromethyl), q = 0, and R^1, R^2, and R^3 are hydrogen. For example, a particularly preferred compound for use in the invention is N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide, having the common name picolinafen, which has been discovered to provide unexpected advantages in the selective control of algae in water bodies. Additional disclosures, preferences and preparative details with regard to compounds of the formula II are found in U.S. Patent No. 5,294,597, which is hereby incorporated herein by reference in its entirety.

Also suitable for use in the present invention are compounds disclosed in U.S. Patent Nos. 4,270,946

issued June 2, 1981, U.S. Patent No. 4,327,218 issued April 27, 1982, and U.S. Patent No. 4,618,366 issued October 21, 1986, and derivatives thereof. Thus, other compounds for use in the invention will be encompassed by the general formula III:



wherein the variables R^1, R^2, R^3, X, Y, q, m, n and Z are as disclosed above. A further preference exists for compounds in which Z is an oxygen atom, m = 2, Y is fluorine (particularly where Y_m represents 2,4-difluoro), n = 1, X is trifluoromethyl (especially where X_n represents 3-trifluoromethyl), q = 0, and R^1, R^2, and R^3 are hydrogen. For example, a particularly preferred compound for use in the invention is N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide, having the common name diflufenican. Additional disclosures, preferences and preparative details with regard to compounds of the formula III are found in U.S. Patent Nos. 4,270,946, 4,327,218, and 4,618,366, each of which is hereby incorporated herein by reference in its entirety.

The algicidal pyridine carboxamide compound may be applied to the body of water in any suitable fashion. Preferably, the compound will be spray-applied to the body of water, in particular to contact algal mass at the surface of the water where such a mass exists. The algicidal pyridine carboxamide will be applied at a level and for a duration sufficient to control the growth of the algal species involved. In this regard, the level and duration of application may vary in accordance with several factors including the particular body of water to be treated, and susceptibility of the algal species to the algicidal compound. In general, the pyridinecarboxamide compound will be maintained in the body of water at a level of about 1 part per billion (ppb) to about 80 ppb, more typically in the range of about 1 ppb to about 30 ppb. The duration of the treatment may vary, for example, from several days to several weeks or more.

It will generally be preferred to adopt a treatment regimen whereby the presence of the pyridinecarboxamide compound has no substantial impact upon native vascular plant life associated with the body of water. For example, the treatment may occur in a body of water containing, and have no substantial impact upon, one or more of the following plants: variable leaf pondweed (*Potamogeton diversifolious*), Illinois pondweed (*Potamogeton illinoensis*), coontail (*Ceratophyllum demeresum*),. Variable leaf milfoil (*Myriophyllum heterophyllum*), cone-spur bladderwort

(*Utricularia gibba*). common elodea (*Elodea canadensis*), spatterdock (*Nuphar luteum*) and water-lily (*Nymphaea* spp.). It will be understood that the particular, native vascular plant or plants will vary depending upon the geographic location of the body of water to be treated.

The present invention also provides algicidal compositions that incorporate a bleaching pyridinecarboxamide compound and a carrier suitable for application to an aquatic environment. In particular preferred carriers will be aqueous-based carriers as known in the art. Compositions of the invention may be provided as algicidal concentrate, for example constituted from about 5% to about 90% by weight of the pyridinecarboxamide compound, more typically about 10% to about 85% by weight of the pyridinecarboxamide compound.

Algicidal compositions of and for use in accordance with the invention may be provided in appropriate containers bearing labels or other indicia for algicidal use, including for example typical label features such as suggested rates of application, activities, etc. In this regard, such compositions may be provided as solid or liquid formulations, including for example wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates or aerosols. In certain forms, in addition to any other carriers included, the

compositions may include an ionic or nonionic surfactant suitable for introduction into an aquatic environment, which may for example facilitate the incorporation of the pyridinecarboxamide compound into the body of water to be treated.

It has also been discovered that bleaching pyridinecarboxamide compounds are effective in controlling a broad spectrum of algal species, including for example *Scenedesmus* and *Ankistrodesmus* (green phytoplankton), *Pithophora* and *Oedogonium* (filamentous green), and *Anabaena*, *Oscillatoria*, and *Pseudanabaena* (blue-green). Such a broad spectrum is important in the use of these compounds has algicides, as a variety of species are encountered in typical water bodies to be treated.

The present invention is applied with advantage to the treatment of water bodies such as lakes, reservoirs, and ponds, where undesirable algal growth is prevalent. As one particular example, relatively small ponds (e.g. of less than about 10 acres) are particularly susceptible to high levels of unwanted algal growth, and can be treated in accordance with the invention. Other water systems susceptible to algal growth may of course also be treated in accordance with the invention.

For the purpose of promoting a further understanding of the present invention and its features

and advantages, the following specific Examples are provided. It will be understood that these Examples are illustrative, and not limiting, in nature.

EXAMPLES

General Methods:

A stock solution of 50 micrograms picolinafen/L was prepared from technical grade picolinafen. Axenic algal cultures of *Scenedesmus* and *Ankistrodesmus* (green phytoplankton), *Pithophora* and *Oedogonium* (filamentous green), and *Anabaena*, *Oscillatoria*, and *Pseudanabaena* (blue-green) were grown. Stock material from these cultures was placed in 250 ml of CLII media (a known, defined algal growth medium). Following the addition of the algae, picolinafen was added to the beakers to achieve concentrations of 0, 1.5, 5, 10, 25, and 50 ppb. Each treatment was replicated three times and beakers were placed in Percival growth chambers that were set at 25°C, with a light intensity of 300 micromoles/square meter/ second and a 16:8 photoperiod. The algae were given a 10 to 14 day incubation period, and depending on the growth form of the algae, either total chlorophyll, cell counts, or algal biomass were quantified as end points.

Results:

Data indicate that most algal species were highly sensitive to Picolinofen at concentrations of 10 ppb and less (see e.g. Tables 1-6). As has been noted with

other phytoene desaturase (PDS) inhibitors, a threshold concentration is achieved at which increasing concentrations no longer provide enhanced efficacy. Visual observations suggest that activity is rapid with bleaching noticed within 12 hours for some of the test species. *Anabaena* proved to show the highest level of tolerance to picolinafen when compared to other algal species (Table 4). The *Anabaena* results may indicate that a longer exposure period may be necessary for this species. Testing of two other blue-green species suggest that this result is more species specific and likely not due to increased tolerance by blue-green algae in general. In addition to the results set forth in Tables 1-6, picolinafen proved to be similarly useful in the control of algal cultures of *Pseudanabaena and Pithophora,* as shown in Tables 7-8. On the other hand, at levels showing significant control of the algal species, picolinafen was found to have substantially no impact upon the growth of hydrilla or eurasian watermilfoil, evidencing the selectivity for algicidal activity over herbicidal activity in the aquatic environment.

Discussion:

Comparing the response to picolinafen for two aquatic macrophyte species to the response of various algal species evidences that picolinafen has greater algacidal than herbicidal activity in the aquatic environment.

Table 1. Impact of Picolinafen on total chlorophyll of *Scenedesmus* following a 10-day exposure period to various concentrations.

Concentration (ppb)	Total Chl (µg chl/g)
Initial values	128 (13)
Untreated	2238 (104)
MeOH Blank	2097 (86)
1.5	2427 (119)
5	87 (16)
10	15 (6)
25	17 (8)
50	12 (6)

Table 2. Impact of Picolinafen on algal cell counts of *Ankistrodesmus* following a 10-day exposure period to various concentrations.

Concentration (ppb)	Cell Count (cells/ml)
Initial values	213,719
Untreated	5,019,444
MeOH Blank	4,877,402
1.5	3,025,323
5	141,246
10	96,622
25	87,012
50	81,706

Table 3. Impact of Picolinafen on total chlorophyll of *Anabaena* following a 10-day exposure period to various concentrations.

Concentration (ppb)	Total Chl (µg chl.)
Initial	132
Untreated	926
MeOH Blank	884
1.5	880
5	906
10	685
25	526
50	101

Table 4. Impact of Picolinafen on total chlorophyll of *Oscillatoria* following a 10-day exposure period to various concentrations.

Concentration (ppb)	Total Chl (µg chl.)
Initial	45
Untreated	582
MeOH Blank	709
1.5	14
5	10
10	21
25	17
50	13

Table 5. Impact of Picolinafen on total chlorophyll and biomass of *Oedogonium* following a 10-day exposure period to various concentrations.

Concentration (ppb)	Total Chl (µg chl.)	Biomass mg dry wt./beaker
Initial	2292	0.007
Untreated	1141	0.067
MeOH Blank	1079	0.066
1.5	1522	0.064
5	1057	0.027
10	342	0.019
25	247	0.011
50	144	0.005

Table 6. Impact of Picolinafen on biomass of *Spirogyra* following a 10-day exposure period to various concentrations.

Concentration (ppb)	Biomass mg dry wt./beaker
Initial	4.6
Untreated	21.3
MeOH Blank	20.6
1.5	16.2
5	6.9
10	3.0
25	3.8
50	3.3

Table 7. Impact of Picolinafin on algal cell counts of *Pseudanabaena* (blue-green) following a 10-day exposure period to various concentrations.

Concentration (ppb)	Cell Count (cells/ml)
Initial Cell Count	890
Untreated	12,511
1.5 ppb	2,344
5 ppb	89
10 ppb	52
25 ppb	98
50 ppb	77

Table 8. Impact of Picolinefin on biomass of *Pithophora* (filamentous green) following a 10-day exposure period to various concentrations.

Concentration (ppb)	Biomass mg dry wt./beaker
Initial Biomass	5.2
Untreated	25.3
1.5 ppb	26.2
5 ppb	19.1
10 ppb	20.4
25 ppb	14.8
50 ppb	11.4